

|   |  |   |  |
|---|--|---|--|
| FORM-PTO-1390<br>(Rev. 12-29-95)  |  | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | ATTORNEY'S DOCKET NUMBER<br>022701-895<br>U S APPLICATION NO (If known, see 37 C.F.R. 1.5)<br>09/674,274 |
| <b>TRANSMITTAL LETTER TO THE UNITED STATES<br/>DESIGNATED/ELECTED OFFICE (DO/EO/US)<br/>CONCERNING A FILING UNDER 35 U.S.C. 371</b>   |  |   |  |
| INTERNATIONAL APPLICATION NO.<br>PCT/FR99/00982   | INTERNATIONAL FILING DATE<br>26 April 1999 | PRIORITY DATE CLAIMED<br>28 April 1998                  |  |
| TITLE OF INVENTION<br>COMPOSITION AND METHOD FOR RADICAL POLYMERISATION OF ETHYLENICALLY UNSATURATED MONOMERS   |  |   |  |
| APPLICANT(S) FOR DO/EO/US<br>Francoise LARTIGUE-PEYROU  |  |   |  |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:   |  |   |  |
| 1. <input type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.<br>2. <input checked="" type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.<br>3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1).<br>4. <input type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.<br>5. <input type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))<br>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).<br>b. <input type="checkbox"/> has been transmitted by the International Bureau.<br>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US)<br>6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).<br>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))<br>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).<br>b. <input type="checkbox"/> have been transmitted by the International Bureau.<br>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.<br>d. <input type="checkbox"/> have not been made and will not be made.<br>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).<br>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).<br>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).<br><b>Items 11. to 16. below concern other document(s) or information included:</b><br>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.<br>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.<br>13. <input type="checkbox"/> A FIRST preliminary amendment.<br><input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.<br>14. <input type="checkbox"/> A substitute specification.<br>15. <input type="checkbox"/> A change of power of attorney and/or address letter.<br>16. <input checked="" type="checkbox"/> Other items or information:<br><b>Petition for Extension of Time</b> |  |   |  |

01/25/2001 EXAMANDO 00000130 09674274

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FORM-PTO-1390  
(Rev. 12-29-99)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

022701-895

U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5)

09/674274

INTERNATIONAL APPLICATION NO.  
PCT/FR99/00982INTERNATIONAL FILING DATE  
26 April 1999PRIORITY DATE CLAIMED  
28 April 1998

## TITLE OF INVENTION

COMPOSITION AND PROCESS FOR THE RADICAL POLYMERIZATION OF ETHYLENICALLY UNSATURATED MONOMERS

## APPLICANT(S) FOR DO/EO/US

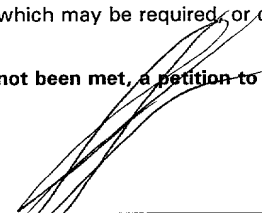
Francoise LARTIGUE-PEYROU

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
   
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

|  |              |   |  |   |              |
|--|--------------|---|--|---|--------------|
| U.S. APPLICATION NO. <b>09/674274</b>  |              | INTERNATIONAL APPLICATION NO.<br>PCT/FR99/00982 |  | ATTORNEY'S DOCKET NUMBER<br><b>022701-895</b> |              |
| 17. <input checked="" type="checkbox"/> The following fees are submitted:  |              |   |  | <b>CALCULATIONS</b>                           | PTO USE ONLY |
| <b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b><br><br>Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1,000.00 (960)<br><br>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$860.00 (970)<br><br>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00 (958)<br><br>International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00 (956)<br><br>International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00 (962) |              |   |  |   |              |
| <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>  |              |   |  |   |              |
| Surcharge of \$130.00 (154) for furnishing the oath or declaration later than 20 <input type="checkbox"/> 30 <input type="checkbox"/> months from the earliest claimed priority date (37 CFR 1.492(e)).  |              |   |  | \$  |              |
| Claims   | Number Filed | Number Extra                                    | Rate   |   |              |
| Total Claims   | 24 -20 =     | 4   | X\$18.00 (966)   | \$ 72.00                                      |              |
| Independent Claims   | 2 -3 =       | 0   | X\$80.00 (964)   | \$ 0  |              |
| Multiple dependent claim(s) (if applicable)  |              |   | + \$270.00 (968)   | \$  |              |
| <b>TOTAL OF ABOVE CALCULATIONS =</b>   |              |   |  | \$ 932.00                                     |              |
| Reduction for 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).  |              |   |  | \$  |              |
| <b>SUBTOTAL =</b>  |              |   |  | \$ 932.00                                     |              |
| Processing fee of \$130.00 (156) for furnishing the English translation later than 20 <input type="checkbox"/> 30 <input type="checkbox"/> months from the earliest claimed priority date (37 CFR 1.492(f)).   |              |   |  | \$  |              |
| <b>TOTAL NATIONAL FEE =</b>  |              |   |  | \$ 932.00                                     |              |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property +   |              |   |  | \$  |              |
| <b>TOTAL FEES ENCLOSED =</b>   |              |   |  | \$ 932.00                                     |              |
|  |              |   |  | <b>Amount to be:</b>                          |              |
|  |              |   |  | <b>refunded</b>                               | \$           |
|  |              |   |  | <b>charged</b>                                | \$           |
|  |              |   |  |   |              |
| a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>932.00</u> to cover the above fees is enclosed.<br>b. <input type="checkbox"/> Please charge my Deposit Account No. <u>02-4800</u> in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.<br>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-4800</u> . A duplicate copy of this sheet is enclosed.   |              |   |  |   |              |
| <b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b>   |              |   |  |   |              |
| SEND ALL CORRESPONDENCE TO:<br><br>Norman H. Stepno<br>BURNS, DOANE, SWECKER & MATHIS, L.L.P.<br>P.O. Box 1404<br>Alexandria, Virginia 22313-1404<br>(703) 836-6620  |              |   |  |   |              |
|  |              |   | <br>_____<br>SIGNATURE |   |              |
|  |              |   | Teresa Stanek Rea<br>_____<br>NAME   |   |              |
|  |              |   | <u>30,427</u><br>_____<br>REGISTRATION NUMBER  |   |              |

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of )  
 )  
Françoise LARTIGUE-PEYROU ) Group Art Unit: Unassigned  
 )  
Application No.: Unassigned ) Examiner: Unassigned  
(Corresponds to PCT/FR99/00982) )  
 )  
International Filing Date: 26 April 1999 )  
 )  
For: COMPOSITION AND PROCESS FOR )  
THE RADICAL POLYMERIZATION )  
OF ETHYLENICALLY )  
UNSATURATED MONOMERS )

**PRELIMINARY AMENDMENT**

**BOX PCT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

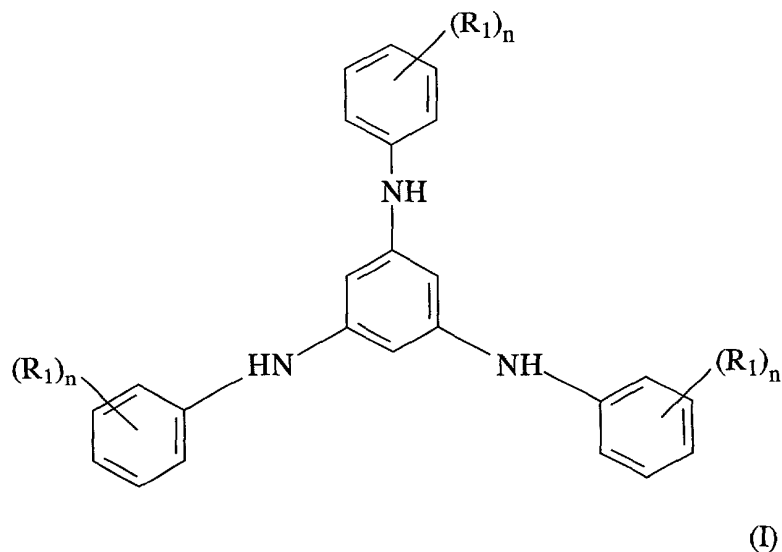
Sir:

Prior to examination, please amend the above-captioned application as follows:

**IN THE CLAIMS:**

Kindly amend the claims as follows:

1. (Amended) Composition [intended to prevent the radical polymerization of ethylenically unsaturated monomers, characterized in that it comprises] comprising ethylenically unsaturated monomers and an effective amount to prevent the radical polymerization of said monomers of at least one [benenetriamine] benenetriamine derivative corresponding to general formula (I):



in said formula (I):

-the identical or different  $R_1$  radicals, represent a hydrogen atom or an [electro-  
doner] electrodonor group,

-the n's, identical or different, represent a number equal to 0, 1 to 5.

Claim 2, line 1, delete "characterized in that" and insert --wherein--;

lines 2-3, delete ", preferably equal to 1 or 2".

Claim 3, line 1, delete "characterized in that" and insert --wherein--;

lines 3-5, delete "preferably 1 to 4 . . . tert-butyl,";

lines 6-7, delete "preferably 2 to 4 carbon atoms such as vinyl, allyl,";

lines 9-11, delete "preferably 1 to 4 carbon . . . phenoxy radical,";

line 18, delete "such as, for example, methylene, ethylene, propylene, isopropylene".

Claim 4, line 1, delete "characterized in that" and insert --wherein--.

Claim 5, line 1, delete "characterized in that" and insert --wherein--.

Claim 6, line 1, delete "one of claims 1 to 5" and insert --claim 1--;

lines 1-2, delete "characterized in that it comprises" and insert --comprising--.

Claim 7, line 1, delete "one of claims 1 to 6" and insert --claim 1--;

lines 1-2, delete "characterized in that, (in the case of an ethylenically unsaturated aromatic monomer) it comprises" and insert --comprising--.

Claim 8, line 1, delete "characterized in that" and insert --wherein--.

lines 3-4, delete ", the. . . 2,4-dinitro-6-sec-butylphenol".

Claim 9, line 1, delete "one of claims 7 and 8" and insert --claim 7--; delete "characterized in that" and insert --wherein--;

line 4, delete ", preferably between 80/20 and 20/80".

Claim 10, line 1, delete "one of claims 1 to 9" and insert --claim 1--;

lines 1-2, delete "characterized in that it further comprises" and insert  
--further comprising--.

Claim 11, line 1, delete "characterized in that" and insert --wherein--;

lines 2-3, delete "such as tert-butyl . . . octylcatechol";

lines 3-7, delete "such as . . . 2,2,3,4,5,5-hexamethylimidazolidine-1-  
oxyl".

Claim 12, line 1, delete "characterized in that" and insert --wherein--;

line 2, before "phenothiazines" insert --and--.

Claim 13, line 1, delete "one of claims 10 to 12" and insert --claim 10--; delete  
"characterized in that" and insert --wherein--;

last line, delete ", preferably 80/20 and 20/80".

Claim 14, line 2, delete "including the addition" and insert --comprising adding--;  
delete "of".

line 11, delete "electro-doner" and insert --electrodonor--

Claim 15, line 1, delete "characterized in that" and insert --wherein--;

lines 2-3, delete ", preferably equal to 1 or 2".

Claim 16, line 1, delete "one of claims 14 and 15" and insert --claim 14--; delete  
"characterized in that" and insert --wherein--;

lines 3-5, delete "preferably 1 to 4 . . . tert-butyl,"

lines 6-7, delete "preferably 2 to 4 . . . allyl,"

lines 9-11, delete "preferably 1 to 4 . . . phenoxy radical,";

lines 17-18, delete "such as, for example, methylene, ethylene,  
propylene, isopropylene".

Claim 17, line 1, delete "characterized in that" and insert --wherein--.

Claim 18, line 1, delete "one of claims 14 to 17" and insert --claim 14--; delete  
"characterized in that" and insert --wherein--;

line 2, delete "comprised";

line 3, delete ", preferably between 5 and 1000 ppm".

Claim 19, line 1, delete "one of claims 14 to 18" and insert --claim 14--; delete  
"characterized in that" and insert --wherein--;

last line, delete "comprised"; delete ", preferably 80/20 and 20/80".

Claim 20, line 1, delete "one of claims 14 to 19" and insert --claim 14--; delete  
"characterized in that" and insert --wherein--;

line 3, delete "comprised";



last line, delete ", preferably 80/20 and 20/80".

Claim 21, line 1, delete "one of claims 14 to 20" and insert --claim 14--; delete  
"characterized in that" and insert --wherein--;

lines 2-4, delete ", preferably selected from . . . acids".

Claim 22, line 1, delete "one of claims 14 to 20" and insert --claim 14--; delete  
"characterized in that" and insert --wherein--;

line 4, after "nitriles;" insert --or--.

Claim 23, line 1, delete "characterized in that" and insert --wherein--;

line 2, after "from" insert --the group consisting of--.

Claim 24, line 1, delete "characterized in that" and insert --wherein--.

#### **REMARKS**

Entry of the foregoing amendment(s) is respectfully requested.

The claims have been amended to eliminate multiple dependency and to place them  
in better condition for U.S. patent practice.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: 

\_\_\_\_\_  
Teresa Stanek Rea  
Registration No. 30,427

P.O. Box 1404  
Alexandria, Virginia 22313-1404  
(703) 836-6620

Date: October 30, 2000

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)**  
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-895

|  |  |                               |                  |
|--|--|-------------------------------|------------------|
| FULL NAME OF SOLE OR FIRST INVENTOR<br>Francoise LARTIGUE-PEYROU |  | SIGNATURE<br><i>Clartigue</i> | DATE<br>23/12/00 |
| RESIDENCE<br>127 bis, rue Pagère, F-69500 Bron, FRANCE           |  | CITIZENSHIP<br>FR             |                  |
| POST OFFICE ADDRESS<br>127 bis, rue Pagère, F-69500 Bron, FRANCE |  |                               |                  |
| FULL NAME OF SECOND JOINT INVENTOR, IF ANY                       |  | SIGNATURE                     | DATE             |
| RESIDENCE  |  | CITIZENSHIP                   |                  |
| POST OFFICE ADDRESS  |  |                               |                  |
| FULL NAME OF THIRD JOINT INVENTOR, IF ANY                        |  | SIGNATURE                     | DATE             |
| RESIDENCE  |  | CITIZENSHIP                   |                  |
| POST OFFICE ADDRESS  |  |                               |                  |
| FULL NAME OF FOURTH JOINT INVENTOR, IF ANY                       |  | SIGNATURE                     | DATE             |
| RESIDENCE  |  | CITIZENSHIP                   |                  |
| POST OFFICE ADDRESS  |  |                               |                  |
| FULL NAME OF FIFTH JOINT INVENTOR, IF ANY                        |  | SIGNATURE                     | DATE             |
| RESIDENCE  |  | CITIZENSHIP                   |                  |
| POST OFFICE ADDRESS  |  |                               |                  |
| FULL NAME OF SIXTH JOINT INVENTOR, IF ANY                        |  | SIGNATURE                     | DATE             |
| RESIDENCE  |  | CITIZENSHIP                   |                  |
| POST OFFICE ADDRESS  |  |                               |                  |
| FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY                      |  | SIGNATURE                     | DATE             |
| RESIDENCE  |  | CITIZENSHIP                   |                  |
| POST OFFICE ADDRESS  |  |                               |                  |
| FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY                       |  | SIGNATURE                     | DATE             |
| RESIDENCE  |  | CITIZENSHIP                   |                  |
| POST OFFICE ADDRESS  |  |                               |                  |

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)**  
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-895

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to the patentability as defined in Title 37, Code of Federal Regulations §1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. §120:

| U.S. APPLICATIONS                     |                  | STATUS (check one)                         |         |           |
|---------------------------------------|------------------|--|---------|-----------|
| U.S. APPLICATION NUMBER               | U.S. FILING DATE | PATENTED                                   | PENDING | ABANDONED |
|                                       |                  |  |         |           |
|                                       |                  |  |         |           |
|                                       |                  |  |         |           |
| PCT APPLICATIONS DESIGNATING THE U.S. |                  |  |         |           |
| PCT APPLICATION NO.                   | PCT FILING DATE  | U.S. APPLICATION NUMBERS ASSIGNED (if any) |         |           |
|                                       |                  |  |         |           |
|                                       |                  |  |         |           |
|                                       |                  |  |         |           |

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

|                           |        |                         |        |                        |        |
|---------------------------|--------|-------------------------|--------|------------------------|--------|
| William L. Mathis         | 17,337 | R. Danny Huntington     | 27,903 | Gerald F. Swiss        | 30,113 |
| Robert S. Swecker         | 19,885 | Eric H. Weisblatt       | 30,505 | Charles F. Wieland III | 33,096 |
| Platon N. Mandros         | 22,124 | James W. Peterson       | 26,057 | Bruce T. Wieder        | 33,815 |
| Benton S. Duffett, Jr.    | 22,030 | Teresa Stanek Rea       | 30,427 | Todd R. Walters        | 34,040 |
| Norman H. Stepno          | 22,716 | Robert E. Krebs         | 25,885 | Ronni S. Jillions      | 31,979 |
| Ronald L. Grudziecki      | 24,970 | William C. Rowland      | 30,888 | Harold R. Brown III    | 36,341 |
| Frederick G. Michaud, Jr. | 26,003 | T. Gene Dillahunt       | 25,423 | Allen R. Baum          | 36,086 |
| Alan E. Kopecki           | 25,813 | Patrick C. Keane        | 32,858 | Steven M. duBois       | 35,023 |
| Regis E. Slutter          | 26,999 | B. Jefferson Boggs, Jr. | 32,344 | Brian P. O'Shaughnessy | 32,747 |
| Samuel C. Miller, III     | 27,360 | William H. Benz         | 25,952 | Kenneth B. Leffler     | 36,075 |
| Robert G. Mukai           | 28,531 | Peter K. Skiff          | 31,917 | Fred W. Hathaway       | 32,236 |
| George A. Hovanec, Jr.    | 28,223 | Richard J. McGrath      | 29,195 |                        |        |
| James A. LaBarre          | 28,632 | Matthew L. Schneider    | 32,814 |                        |        |
| E. Joseph Gess            | 28,510 | Michael G. Savage       | 32,596 |                        |        |



and:

Address all correspondence to:



**21839**

Norman H. Stepno  
BURNS, DOANE, SWECKER & MATHIS, L.L.P.  
P.O. Box 1404  
Alexandria, Virginia 22313-1404

Address all telephone calls to: Norman H. Stepno at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**  
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-895

As a below named inventor, I hereby declare that:  
My residence, post office address and citizenship are as stated below next to my name;  
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**COMPOSITION AND PROCESS FOR THE RADICAL POLYMERIZATION OF ETHYLENICALLY**

**UNSATURATED MONOMERS**

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Number \_\_\_\_\_  
on \_\_\_\_\_  
and was amended  
on \_\_\_\_\_ (if applicable).

☒ was filed as PCT international application

Number PCT/FR99/00982  
on 26 April 1999  
and was amended  
on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

**PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §119:**

| COUNTRY<br>(if PCT, indicate "PCT") | APPLICATION NUMBER | DATE OF FILING<br>(day, month, year) | PRIORITY CLAIMED<br>UNDER 35 U.S.C. §119 |
|-------------------------------------|--------------------|--------------------------------------|--|
| FRANCE                              | 98/05317           | 28 April 1998                        | <u>X</u> Yes    _ No                     |
|                                     |                    |                                      | _ Yes    _ No                            |
|                                     |                    |                                      | _ Yes    _ No                            |
|                                     |                    |                                      | _ Yes    _ No                            |
|                                     |                    |                                      | _ Yes    _ No                            |

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

|                               |                        |
|-------------------------------|------------------------|
| _____<br>(Application Number) | _____<br>(Filing Date) |
| _____<br>(Application Number) | _____<br>(Filing Date) |

COMPOSITION AND PROCESS FOR THE RADICAL POLYMERIZATION OF  
ETHYLENICALLY UNSATURATED MONOMERS

An object of the present invention is a composition which can be used as an  
5 inhibitor of the radical polymerization of ethylenically unsaturated monomers and a  
process for preventing the radical polymerization of such unsaturated monomers  
during their industrial preparation. It relates in particular to vinyl aromatic monomers.

Ethylenically unsaturated monomers are liable to polymerize spontaneously  
10 under the action of heat. Thus, premature polymerization must be avoided during  
production, purification and storage of said monomers. During production or  
purification, premature polymerization is detrimental as it causes a drop in production  
yields and clogs up machinery, often making it necessary to stop production  
temporarily for maintenance, leading to a production surcharge. Due to the  
15 exothermicity of the polymerization reaction, explosions and fires are also of concern.

The distillation of certain ethylenically unsaturated monomers is particularly  
problematic as high temperatures must be used: this applies in particular to the  
distillation of vinylaromatic derivatives such as styrene, l'-methylstyrene and other  
vinylbenzenes.

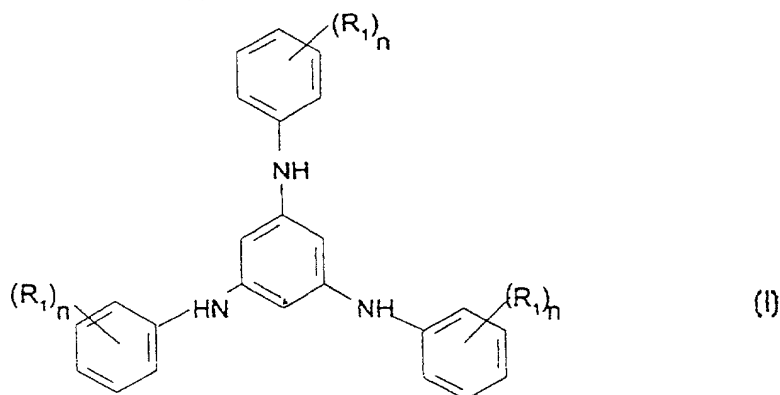
20 To prevent the polymerization of ethylenically unsaturated monomers, it is  
known in the state of the art to add one or more polymerization inhibitors or retarders,  
either in a preventative manner in the course of production or also directly to the said  
monomers before using them.

Thus, to inhibit the polymerization of styrene during its production, industry  
25 currently uses 2,4-dinitrophenol, 4,6-dinitro-o-cresol (DNOC), 2,6-dinitro-p-cresol  
(DNPC) [US 4 105 506] or also 2,4-dinitro-6-sec-butylphenol (DNBP). The Patent  
US 4 466 905 demonstrates that the combinations of 2,6-dinitro-p-cresol with p-  
phenylene diamine compounds or with tert-butylcatechol are very effective at limiting  
the polymerization of styrene if a minimum amount of oxygen is present. In JP 63  
30 316745, the possibility of using 2-methyl-4-nitrosophenol in combination with 2,6-  
dinitro-p-cresol is indicated.

In general, the nitrophenolic inhibitors of the state of the art are relatively  
toxic and are not always very stable.

An object of the invention is to provide a composition for preventing premature polymerization of ethylenically unsaturated monomers during the production of said monomers.

An object of the present invention is therefore a composition intended to prevent the radical polymerization of ethylenically unsaturated monomers characterized in that it comprises at least one benzenetriamine derivative corresponding to general formula (I):



in said formula (I):

- the identical or different  $R_1$  radicals represent a hydrogen atom or an electro-doner group,
- the  $n$ 's, identical or different, represent a number equal to 0, 1 to 5.

A variation of the invention consists of combining the benzenetriamine derivative of the invention with one or several vehicles which are compatible with said monomer and with each of the constituents of the composition.

Another variation of the invention is to combine it with another polymerization inhibitor.

A compound corresponding to formula (I) in which the  $R_1$  radical or radicals represent an electro-doner group is included in the composition of the invention.

In the present text, by "electro-doner group" is meant a group as defined by H.C. Brown in Jerry MARCH's work – Advanced Organic Chemistry, chapter 9, pages 243 and 244 (1985).

The following can be mentioned as examples of preferred  $R_1$  electro-doner groups:

-a linear or branched alkyl radical, having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl,

-a linear or branched alkenyl radical, having 2 to 6 carbon atoms, preferably 2 to 4 carbon atoms such as vinyl, allyl,

-a linear or branched alkoxy or thioether radical, having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy, isopropoxy, butoxy radicals, an alkenyloxy radical, preferably an allyloxy radical or a phenoxy radical,

-a radical of formula:

10                                 $-R_2-OH$   
                                       $-R_2-SH$   
                                       $-R_2-N-(R_3)_2$

in said formulae  $R_2$  represents a valency bond or a linear or branched, saturated or unsaturated divalent hydrocarbon radical, having 1 to 6 carbon atoms such as, for example, methylene, ethylene, propylene, isopropylene, isopropylidene; the identical or different  $R_3$  radicals, represent a hydrogen atom or a linear or branched alkyl radical, having 1 to 6 carbon atoms.

In formula (I),  $n$  is a number preferably less than or equal to 4, preferably equal to 1 or 2.

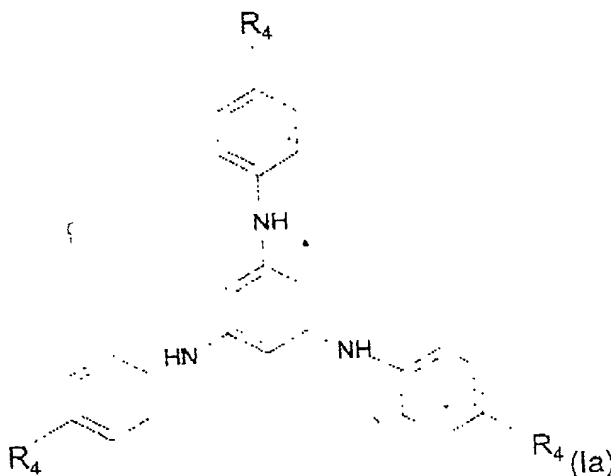
20            The invention only excludes the three benzene rings carrying  $R_1$  radicals of a different nature and whose number  $n$  is different.

Among the benzenetriamine derivatives of formula (I), certain are particularly preferred and in particular those corresponding to formula (Ia):

25

30

in said formula (Ia):





-the identical or different  $R_4$  radicals, represent a hydroxyl group or a linear or branched alkyl or alkoxy radical, having 1 to 4 carbon atoms.

Among the compounds of formula (Ia), those which correspond to the formula (I) in which  $R_1$  represents a hydroxy group or methoxy group or a methyl group are preferably used.

N,N',N''-tri(p-methoxyphenyl)-1,3,5-benzenetriamine and N,N',N''-tri(p-methylphenyl)-1,3,5-benzenetriamine are preferably chosen.

A mixture of benzenetriamine derivatives can also be used.

Thus, the compositions of the invention comprising at least one benzenetriamine derivative of formula (Ia) constitute a particularly preferred embodiment of the invention.

Certain benzenetriamine derivatives of formula (I) are commercially available. The others are easily prepared by a person skilled in the art using commercially-available products.

The compositions of the invention are suitable for the stabilization of any monomer having at least one ethylenic unsaturation.

Ethylenically unsaturated monomers comprise more precisely ethylenically unsaturated aromatic monomers such as styrene,  $\alpha$ -methylstyrene, divinylbenzene, vinyltoluene, vinylnaphthalene, styrene sulphonics acids, etc.

Ethylenically unsaturated monomers also comprise olefinic monomers comprising one or two unsaturations such as isoprene and butadiene; unsaturated halogenated monomers of vinyl chloride, chloroprene, vinylidene fluoride, vinylidene chloride and vinyl fluoride type; unsaturated acids of acrylic acid, methacrylic acid and crotonic acid type; unsaturated esters, in particular unsaturated acrylic acid esters of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate type; unsaturated methacrylic acid esters of methyl methacrylate, butyl methacrylate, lauryl methacrylate, dimethylaminoethyl methacrylate, stearyl methacrylate, vinyl acetate type; unsaturated resins such as for example acrylated epoxy resins and polyethylene glycol diacrylate; unsaturated amides such as acrylamide, N,N-dimethylacrylamide, methylene bisacrylamide and N-vinylpyrrolidone; unsaturated nitriles of acrylonitrile type; unsaturated ethers such as vinyl and methyl ether; vinylpyridines; diethyl vinylphosphonate and sodium styrene sulphonate. It should be understood that this list

is in no way exhaustive, the invention relates in a general manner to the stabilization of all types of ethylenically unsaturated aliphatic monomers.

Nevertheless, the compositions of the invention are particularly effective for the stabilization of ethylenically unsaturated aromatic monomers, in particular vinylaromatic monomers such as styrene,  $\alpha$ -methylstyrene, divinylbenzene, vinyltoluene, styrene sulphonic acids.

The invention preferably applies to styrene.

The compositions of the invention form either true solutions, i.e. constituted by perfectly miscible ingredients, or emulsions or also suspensions. According to a preferred embodiment, the compositions are in the form of true solutions.

The presence in the composition of one or more vehicles is optional. It can prove necessary, however, when the solubility of the benzenetriamine derivatives of the composition in the monomer to be stabilized is low, indeed insufficient. In this case in fact, it is preferable to incorporate into the composition one or more vehicles which are compatible on the one hand with the monomer to be stabilized and on the other hand with each of the other constituents of the composition. By "compatible" is meant according to the invention a vehicle which is chemically inert vis-à-vis the different ingredients of the composition and the monomer. The nature of the vehicle therefore depends on the different constituents present as well as the nature of the monomer itself.

When the monomer is a vinyl aromatic derivative, particularly appropriate vehicles are benzene, toluene, xylene, ethylbenzene, styrene, acetophenone, methylphenylcarbinol or mixtures of these solvents. In this case, ethylbenzene is preferably used.

Depending on the nature of the monomer, a person skilled in the art will easily determine the combination of the benzenetriamine derivative and solvents which gives the best results.

According to the invention, it is possible to combine the benzenetriamine derivative with other standard compounds used as polymerization retarders or other polymerization inhibitors.

The choice of these is easily determined by a person skilled in the art. It depends on the nature of the polymer. Examples are given hereafter but are in no way limitative.

In the case of an ethylenically unsaturated aromatic monomer, the compositions according to the invention advantageously contain one or more nitroaromatic derivatives. Such compounds are known in the state of the art as polymerization retarders. It is also known to combine them with polymerization inhibitors. Specifically, the polymerization inhibitor prevents polymerization up to a certain time beyond which the polymerization reaction starts as normal. This time is the induction time. The longer the induction time, the more effective the inhibition. The role of the retarder is different. It does not prevent the polymerization but slows down the polymerization kinetics. A more or less significant synergy is observed in the combination of an inhibitor with a retarder. Thus, the compositions of the invention containing at least one polymerization retarder and at least one polymerization inhibitor form a preferred subject of the invention.

The nitroaromatic derivative is advantageously selected from 1,3-dinitrobenzene, 1,4-dinitrobenzene, 2,6-dinitro-4-methylphenol, 2-nitro-4-methylphenol, 2,4-dinitro-1-naphthol, 2,4,6-trinitrophenol (picric acid), 2,4-dinitro-6-methylphenol, 2,4-dinitrochlorobenzene, 2,4-dinitrophenol, 2,4-dinitro-6-sec-butylphenol, 4-cyano-2-nitrophenol and 3-iodo-4-cyano-5-nitrophenol.

2,6-dinitro-4-methylphenol, 2,4-dinitro-6-methylphenol, 2,4-dinitrophenol and 2,4-dinitro-6-sec-butylphenol are preferably used, 2,4-dinitro-6-sec-butylphenol being particularly advantageous.

The nitroaromatic derivatives are added to the composition so that the ratio of the total mass of the constituents of benzenetriamine type of formula (I) to the total mass of the nitroaromatic-type constituents is comprised between 90/10 and 10/90, preferably between 80/20 and 20/80, better still between 60/40 and 40/60. This weight ratio is calculated by determining the ratio of the total quantity (by weight) of the benzenetriamine derivatives of formula (I) present in the composition to the total quantity (by weight) of the nitroaromatic derivatives of the composition.

According to a variation of the invention, the compositions of the invention can contain other polymerization inhibitors such as alkylated phenols such as tert-butylcatechol, 2,5-di-tert-octylhydroquinone, 3,5-di-tert-octylcatechol; compounds of nitroxide type such as 2,2,6,6-tetramethylpiperidine-N-oxyl, 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl, 4-oxo-2,2,6,6-tetramethylpiperidine-N-oxyl; 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl; imidazolidines/imidazolines-N-oxyl as described in FR 97/04230, preferably 2,2,3,4,5,5-hexamethylimidazolidine-1-oxyl or

any other inhibitors known in the state of the art provided that they are compatible with the other ingredients of the composition under the operating conditions to which the monomer to be stabilized is subjected.

In the case of an ethylenically unsaturated aliphatic monomer, it is also possible to use other inhibitors such as hydroquinone, p-methoxyphenol, phenothiazines.

The standard polymerization inhibitor or inhibitors are added to the composition such that the ratio of the total mass of the constituents of benzenetriamine type of formula (I) to the total mass of the other inhibitors is comprised between 90/10 and 10/90, preferably between 80/20 and 20/80, better still between 60/40 and 40/60.

The compositions of the invention are easily prepared by mixing the different constituents in the selected vehicle.

Another object of the invention is a process allowing the prevention of the radical polymerization of an ethylenically unsaturated monomer preferably a vinyl aromatic monomer. This process comprises, for example, the addition to said monomer of an effective quantity of a composition of the invention as defined above.

The quantity of benzenetriamine derivative to be added in order to obtain an effective inhibition of the polymerization varies greatly. It is a function of the monomer to be stabilized and operating conditions to which this monomer is subjected. It is clear that at high temperatures, the quantity of inhibitor becomes more significant. The process of the invention is in fact applicable for the stabilization of the monomer during production and purification. Therefore, it is common for the purification to be carried out by distillation of the monomer, the temperature at boiling point being able to exceed 120°C.

Thus, the ideal quantity of inhibitor must be evaluated case by case.

Whatever this may be, by way of indication, a total quantity of benzenetriamine derivative comprised between 1 and 2000 ppm, preferably between 5 and 1000 ppm generally suffices, this quantity being expressed relative to the total weight of the monomer to be stabilized.

As indicated previously, it is desirable to add to the ethylenically unsaturated aromatic monomer an effective quantity of one or more nitroaromatic derivatives as a polymerization retarder. As a preferred retarder, 2,6-dinitro-4-methylphenol, 2,4-

dinitro-6-methylphenol and 2,4-dinitrophenol, but above all 2,4-dinitro-6-sec-butylphenol can be mentioned again.

The proportion of the nitroaromatic-type retarder or retarders is preferably such that the ratio of the total mass of the benzenetriamine-type constituents of formula (I) to the total mass of nitroaromatic-type constituents is comprised between 90/10 and 10/90, better still between 80/20 and 20/80. This weight ratio is calculated by determining the ratio of the total quantity (by weight) of benzenetriamine derivatives of formula (I) present in the composition to the total quantity (by weight) of nitroaromatic derivatives of the composition.

As previously indicated, it is possible to add one or more known polymerization inhibitors to the monomer.

The proportion of the polymerization inhibitor or inhibitors is preferably such that the ratio of the total mass of constituents of benzenetriamine derivative type of formula (I) to the total mass of other inhibitors is comprised between 90/10 and 10/90, better still between 80/20 and 20/80.

The benzenetriamine derivative according to the invention, optionally combined with a nitroaromatic derivative or other standard polymerization inhibitors can be added to the monomer in a completely conventional manner. The point of introduction, in the case of a distillation, is very variable: it can be envisaged to add each of these compounds at the level of heat exchangers, pipes, pumps, boilers, compressors or more generally containers. It should be understood that the addition can be carried out continuously or also repeated over time at one or different specific sites.

According to the invention, it is possible to envisage the simultaneous or separate addition of the inhibitor of the invention and/or the retarder and/or the other inhibitor.

The process of the invention is particularly advantageous in terms of the effectiveness of inhibition of the radical polymerization of aromatic vinyl monomers.

The following examples are given by way of illustration and relate to the preferred embodiments of the invention.

#### EXAMPLES OF USE ON AROMATIC VINYL MONOMERS

### Example 1

#### Comparison Example 1a

In order to evaluate the inhibition properties of the products of the invention referenced vis-à-vis the radical polymerization of vinyl monomers, inhibition tests with styrene were carried out with the following operating protocol.

Before each test, the styrene used (marketed by Merck) is first destabilized by passing it over an activated alumina column (obtained from Procatalyse) in order to completely eliminate the tert-butylcatechol initially present at a rate of 15-20 ppm.

The resulting styrene (10 ml) is placed in a test tube and the adequate quantity of inhibitor is then added.

Argon is introduced in the liquid phase of the reactor by bubbling through (5 mins) as well as in the top of the reactor by bubbling through (5 mins).

The tube is closed and placed in an oil bath thermostatically controlled at 100°C for 2 hours.

The amount of polymer formed after 2 hours is determined by the precipitation process from methanol.

To this end, a cooled-down sample of 10 ml of styrene is decanted into a glass flask containing approximately 50 ml of methanol in order to precipitate the polystyrene formed which is insoluble in the methanol.

The precipitate is then filtered on a milliporous filter then the residue is dried in a stove at 40°C before being weighed.

The results of the tests are summarized in Table (I).

Table (I)

| Ref. ex. | Inhibitor   | Content relative to the styrene (ppm) | Amount of polymer formed |
|----------|---|---------------------------------------|--------------------------|
| 1a       | no inhibitor  | 0                                     | 5.72                     |
| 1        | N,N',N''-tri(p-methoxyphenyl)-1,3,5-benzenetriamine | 100                                   | 0                        |

The results show that the benzenetriamine derivatives are excellent inhibitors of the polymerization of styrene.

## EXAMPLES OF USE ON UNSATURATED ALIPHATIC MONOMERS

In order to evaluate the inhibitory properties of the products of the invention  
 5 vis-à-vis the radical polymerization of unsaturated aliphatic monomers, inhibition  
 tests with methyl methacrylate were carried out with the following operating protocol.

The effectiveness of an inhibitor according to the invention (or a mixture of  
 inhibitors including at least one inhibitor according to the invention) for methyl  
 methacrylate is determined by measuring the induction time which represents the time  
 10 at the end of which the monomer starts to polymerize when it is heated in a bath at  
 regulated temperature and in the presence of an initiator. This time is determined by a  
 slight exothermicity of the sample studied.

The measures are carried out in a laboratory calorimeter, the time and  
 temperature parameters are recorded and transferred to a microcomputer.

15 The tests were carried out with methyl methacrylate (MMA) previously  
 destabilized by passing over an activated alumina column in order to completely  
 eliminate the p-methoxyphenol (initial stabilizing agent) from the medium.

20 ml of MMA restabilized with 20 ppm of the inhibitor to be tested is  
 introduced into a test tube then 100 ppm of azobisisobutyronitrile (AIBN) initiator is  
 20 introduced. The tube is immersed in a bath thermostatically controlled at 80°C and the  
 difference in temperature between this sample and a reference tube containing  
 silicone fluid is recorded continuously. The induction time  $T_i$  corresponds to the  
 visible exothermicity which indicates the start of the MMA polymerization. The curve  
 T as a function of time is recorded continuously. The greater the induction time, the  
 25 more effective the inhibitor tested is at a constant weight concentration.

The following Table (II) shows the induction time values of some "standard"  
 industrial (meth)acrylate inhibitors.

Table (II)

| Inhibitors          | Induction time $T_i$ (min) |
|---------------------|----------------------------|
| phenothiazine (PTZ) | 26                         |
| hydroquinone (HQ)   | 55                         |

Examples 2 and 3

The operating protocol given above is repeated for each polymerization inhibitor.

Table (III) summarizes the results obtained over the induction times for  
5 different inhibitors of the invention.

Table (III)

| ref. ex. | Polymerization inhibitors                           | Induction time Ti (min) of<br>MMA |
|----------|---|-----------------------------------|
| 2        | N,N',N''-tri(p-methylphenyl)-1,3,5-benzenetriamine  | 70                                |
| 3        | N,N',N''-tri(p-methoxyphenyl)-1,3,5-benzenetriamine | 53                                |

The induction time values are better than or equivalent to hydroquinone which is currently one of the best industrial inhibitors for the (meth)acrylates industry.

10

Example 4

In this example, the combination of N,N',N''-tri(p-methoxyphenyl)-1,3,5-benzenetriamine of the invention with another inhibitor is described.

In the test, 20 ml MMA + 100 ppm AIBN + a mixture of inhibitors: 10 ppm  
15 hydroquinone (HQ) + 10 ppm inhibitor of the invention are used.

Table (IV) summarizes the results obtained over the induction time for the mixture of the inhibitors of the invention.

Table (IV)

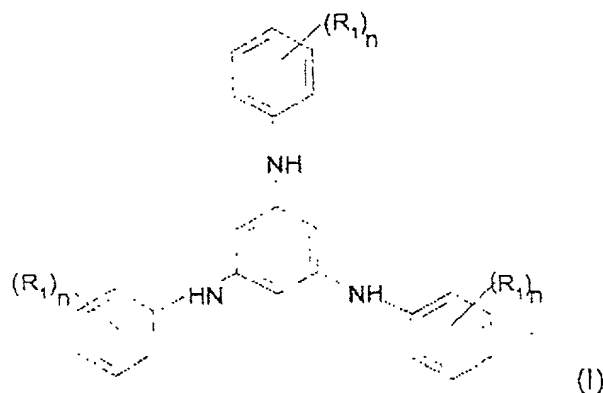
| Ref. ex. | Inhibitor  | Induction time Ti (min) of<br>MMA |
|----------|--|-----------------------------------|
| 4        | HQ + N,N',N''-tri(p-methoxyphenyl)-1,3,5-benzenetriamine | 65                                |

20



CLAIMS

1. Composition intended to prevent the radical polymerization of ethylenically unsaturated monomers, characterized in that it comprises at least one benzenetriamine derivative corresponding to general formula (I):



in said formula (I):

- the identical or different  $R_1$  radicals, represent a hydrogen atom or an electro-doner group,

-the n's, identical or different, represent a number equal to 0, 1 to 5.

2. Composition according to claim 1, characterized in that the benzenetriamine derivative corresponds to formula (I) in which n is a number less than or equal to 4, preferably equal to 1 or 2.

3. Composition according to claim 1, characterized in that the benzenetriamine derivative corresponds to formula (I) in which  $R_1$  represents:

.a linear or branched alkyl radical, having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl,

.a linear or branched alkenyl radical, having 2 to 6 carbon atoms, preferably 2 to 4 carbon atoms such as vinyl, allyl,

.a linear or branched alkoxy or thioether radical, having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy, isopropoxy, butoxy radicals, an alkenyloxy radical, preferably an allyloxy radical or a phenoxy radical,

.a radical of formula:

-R<sub>2</sub>-OH

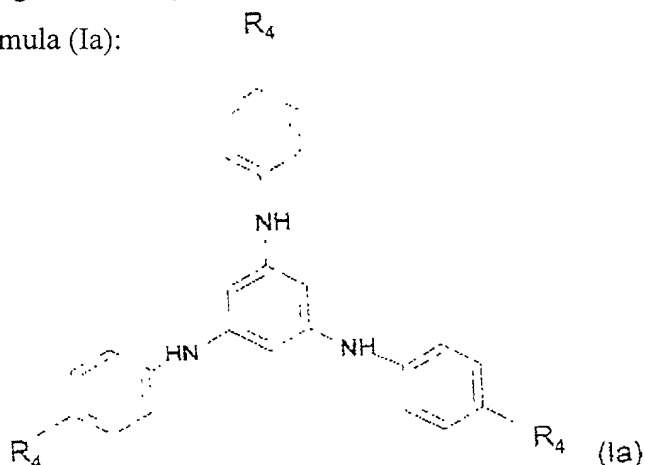
-R<sub>2</sub>-SH

-R<sub>2</sub>-N-(R<sub>3</sub>)<sub>2</sub>

5 in which formulae R<sub>2</sub> represents a valency bond or a linear or branched, saturated or unsaturated divalent hydrocarbon radical having 1 to 6 carbon atoms such as, for example, methylene, ethylene, propylene, isopropylene; the identical or different R<sub>3</sub> radicals, represent a hydrogen atom or a linear or branched alkyl radical having 1 to 6 carbon atoms.

10

4. Composition according to claim 1, characterized in that the benzenetriamine derivative corresponds to formula (Ia):



15

20

in said formula (Ia):

-the identical or different R<sub>4</sub> radicals, represent a hydroxyl group or a linear or branched alkyl or alkoxy radical having 1 to 4 carbon atoms.

25

5. Composition according to claim 1, characterized in that the benzenetriamine derivative is N,N',N''-tri(p-methoxyphenyl)-1,3,5-benzenetriamine and N,N',N''-tri(p-methylphenyl)-1,3,5-benzenetriamine.

30

6. Composition according to one of claims 1 to 5, characterized in that it comprises one or more solvents selected from benzene, toluene, xylene, ethyl benzene, styrene, acetophenone and methylphenylcarbinol as a vehicle.

7. Composition according to one of claims 1 to 6, characterized in that, (in the case of an ethylenically unsaturated aromatic monomer) it comprises at least one nitroaromatic derivative.

8. Composition according to claim 7, characterized in that the nitroaromatic derivative is selected from 2,6-dinitro-4-methylphenol, 2,4-dinitro-6-methylphenol, 2,4-dinitrophenol, 2,4-dinitro-6-sec-butylphenol and 2,4-nitro-4-methylphenol, the  
5 nitroaromatic derivative being preferably 2,4-dinitro-6-sec-butylphenol.

9. Composition according to one of claims 7 and 8, characterized in that the ratio of the total mass of benzenetriamine derivative of formula (I) constituents to the total mass of nitroaromatic derivative type constituents is comprised between 90/10 and  
10 10/90, preferably between 80/20 and 20/80.

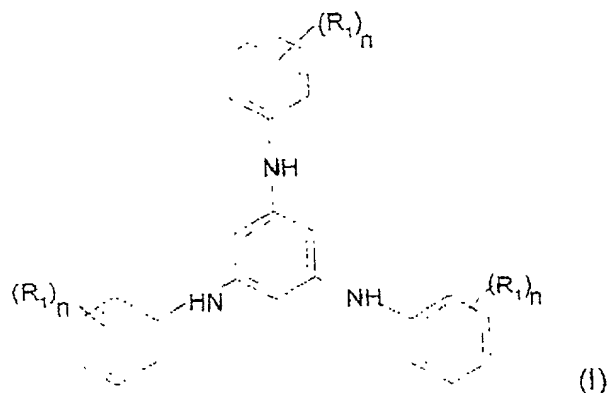
10. Composition according to one of claims 1 to 9, characterized in that it further comprises another polymerization inhibitor.

11. Composition according to claim 10, characterized in that the polymerization inhibitor is selected from the alkylated phenols such as tert-butyl-catechol, 2,5-di-tert-octylhydroquinone, 3,5-di-tert-octylcatechol; compounds of nitroxide type such as 2,2,6,6-tetramethylpiperidine-N-oxyl, 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl, 4-oxo-2,2,6,6-tetramethylpiperidine-N-oxyl; 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl; imidazolidines/imidazolines-N-oxyl, preferably  
20 2,2,3,4,5,5-hexamethylimidazolidine-1-oxyl or any other known inhibitor.

12. Composition according to claim 10, characterized in that the polymerization inhibitor is hydroquinone; p-methoxyphenol; phenothiazines, in the case of an  
25 ethylenically unsaturated aliphatic monomer.

13. Composition according to one of claims 10 to 12, characterized in that the quantity of polymerization inhibitor is such that the ratio of the total mass of the benzenetriamine derivative type of formula (I) constituents to the total mass of the  
30 other inhibitors is comprised between 90/10 and 10/90, preferably 80/20 and 20/80.

14. Process intended to prevent the radical polymerization of an ethylenically unsaturated monomer including the addition to said monomer of an effective quantity of at least one benzenetriamine derivative corresponding to general formula (I):



10 in said formula (I):

- the identical or different  $R_1$  radicals, represent a hydrogen atom or an electro-doner group,

-the n's, identical or different, represent a number equal to 0, 1 to 5.

15 15. Process according to claim 14, characterized in that the benzenetriamine derivative corresponds to formula (I) in which n is a number less than or equal to 4, preferably equal to 1 or 2.

20 16. Process according to one of claims 14 and 15, characterized in that the benzenetriamine derivative corresponds to formula (I) in which  $R_1$  represents:

.a linear or branched alkyl radical, having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl,

25 .a linear or branched alkenyl radical, having 2 to 6 carbon atoms, preferably 2 to 4 carbon atoms such as vinyl, allyl,

.a linear or branched alkoxy or thioether radical, having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy, isopropoxy, butoxy radicals, an alkenyloxy radical, preferably an allyloxy radical or a phenoxy radical,

30 .a radical of formula:

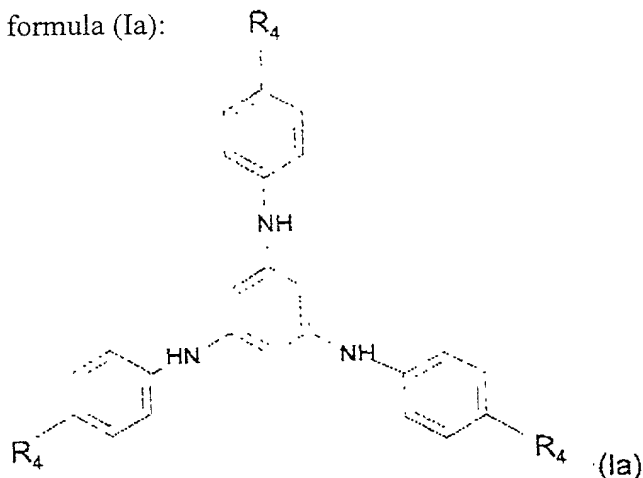
- $R_2$ -OH

- $R_2$ -SH

- $R_2$ -N-( $R_3$ )<sub>2</sub>

in said formulae  $R_2$  represents a valency bond or a linear or branched, saturated or unsaturated divalent hydrocarbon radical having 1 to 6 carbon atoms such as, for example, methylene, ethylene, propylene, isopropylene; the identical or different  $R_3$  radicals represent a hydrogen atom or a linear or branched alkyl radical having 1 to 6 carbon atoms.

17. Process according to claim 14, characterized in that the benzenetriamine derivative corresponds to formula (Ia):



in said formula (Ia):

-the identical or different  $R_4$  radicals, represent a hydroxyl group or a linear or branched alkyl or alkoxy radical having 1 to 4 carbon atoms.

18. Process according to one of claims 14 to 17, characterized in that the total quantity of the benzenetriamine derivative of formula (I) added is comprised between 1 and 2000 ppm, preferably between 5 and 1000 ppm relative to the total weight of said monomer.

19. Process according to one of claims 14 to 18, characterized in that the quantity of nitroaromatic type derivative is such that the ratio of the mass of benzenetriamine type derivatives of formula (I) to the total mass of nitroaromatic-type constituents is comprised between 90/10 and 10/90, preferably 80/20 and 20/80.

20. Process according to one of claims 14 to 19, characterized in that the quantity of polymerization inhibitor is such that the ratio of the mass of benzenetriamine-type derivatives of formula (I) to the total mass of the other inhibitors is comprised between 90/10 and 10/90, preferably between 80/20 and 20/80.

21. Process according to one of claims 14 to 20, characterized in that said ethylenically unsaturated monomer is a vinylaromatic monomer, preferably selected from styrene,  $\alpha$ -methylstyrene, vinyltoluene, divinylbenzene and styrenesulphonic acids.

22. Process according to one of claims 14 to 20, characterized in that said ethylenically unsaturated aliphatic monomer is selected from olefinic monomers comprising one or two unsaturations; unsaturated halogenated monomers; unsaturated acids; unsaturated esters; unsaturated resins; unsaturated amides; unsaturated nitriles; unsaturated ethers.

23. Process according to claim 22, characterized in that said ethylenically unsaturated aliphatic monomer is selected from isoprene and butadiene; vinyl chloride, chloroprene, vinylidene chloride, vinylidene fluoride and vinyl fluoride acrylic acid, methacrylic acid and crotonic acid; unsaturated acrylic acid esters of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate type; unsaturated methacrylic acid esters of methyl methacrylate, butyl methacrylate, lauryl methacrylate, dimethylaminomethyl methacrylate, stearyl methacrylate type; vinyl acetate; acrylated epoxy resins and polyethyleneglycol diacrylate; acrylamide, N,N-dimethylacrylamide, methylenebisacrylamide and N-vinylpyrrolidone; acrylonitrile; vinyl and methyl ether; vinylpyridines; diethyl vinylphosphonate and sodium styrene sulphonate.

24. Process according to claim 23, characterized in that said aliphatic monomers are esters of acrylic acid and methacrylic acid.